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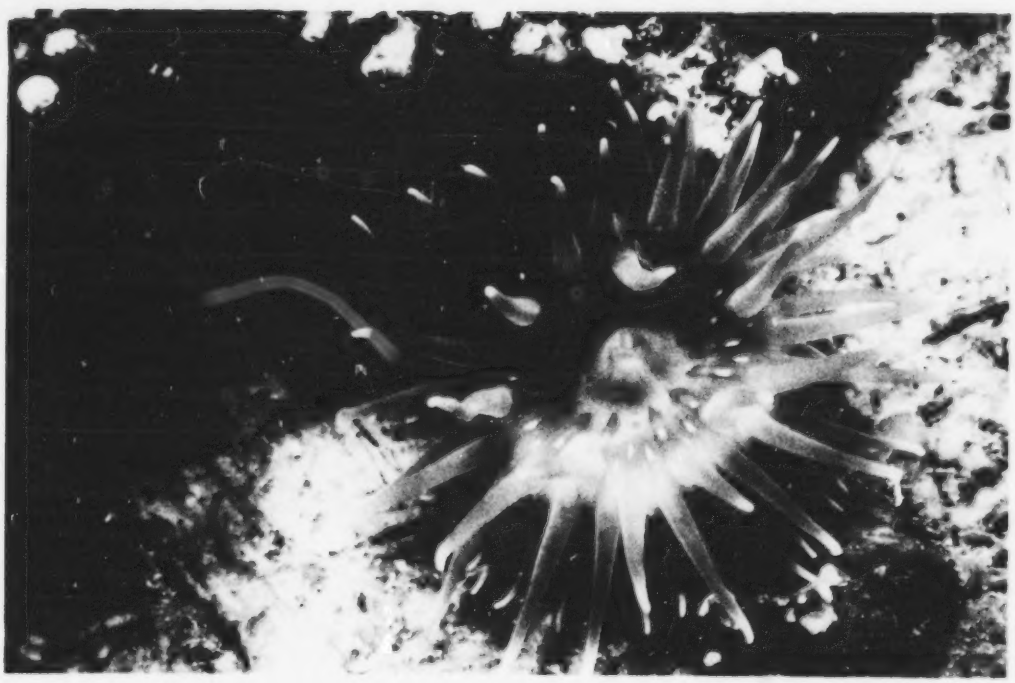
A METHOD TO MEASURE SEDIMENT – WATER TRACE METAL FLUXES: A FIELD EVALUATION IN HALIFAX HARBOUR OCEAN DUMPING REPORT 7

B.T. Hargrave and S. MacKnight



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A METHOD TO MEASURE SEDIMENT-WATER TRACE METAL FLUXES: A FIELD EVALUATION IN HALIFAX HARBOUR

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ABSTRACT

Dissolved trace metals were concentrated from seawater pumped from outside (ambient) and within (supernatant) benthic chambers placed over undisturbed sediment to determine fluxes to and from sediments at two sites in Halifax Inlet. Benthic chambers enclosing 17.6 L of supernatant water over 0.145 m^2 of sediment were fitted with battery-operated pumps that drew seawater through 0.45 µm filters and ion exchange columns (8-hydroxyquinoline immobilized on polystyrene XE-305 resin). Trace metal concentrations adsorbed to columns, corrected for incubation time and volume pumped, were used to calculate influx (ambient>supernatant concentration) or efflux (supernatant>ambient concentration) rates for dissolved metals. The aluminum chambers were found to contaminate seawater with Cd and Cu. Net fluxes (µg m^{-2} h^{-1}) of Fe (72 to 287), Mn (5 to 120) and Zn (-134 to 63) from sediments were measured when surface sediments were partially or wholly anoxic. Ni, Cd and Cu were also leached from sediments into overlying water but rates were low (<10 µg m^{-2} h^{-1}) and variable. Complexation of Cu with organic matter in seawater and sediment pore water resulted in poor extraction efficiency by XE-305 columns but release of uncomplexed Cu occurred when dissolved oxygen was depleted over reduced sediments. All other dissolved metals were extracted with >75% efficiency. Ranges of metal efflux rates from sediments in Halifax Inlet are similar to values measured in Narragansett Bay.

RESUME

On a concentré les métaux-traces dissous dans de l'eau de mer provenant de l'extérieur (eau ambiante) et de l'intérieur (eau surnageante) d'enceintes benthiques déposées sur des sédiments non perturbés, en vue de déterminer les échanges avec les sédiments à deux endroits dans le port d'Halifax. Les enceintes benthiques qui contenaient 17,6 L d'eau reposant sur 0,145 m^2 de sédiments étaient munies de pompes, alimentées par des batteries, qui aspiraient l'eau de mer à travers des filtres de 0,45 µm et des colonnes échangeuses (8-hydroxyquinoléine immobilisée sur une résine de polystyrène XE-305). La concentration des métaux-traces adsorbés sur la résine échangeuse, corrigée pour tenir compte du temps d'incubation et du volume pompé, a été utilisée pour calculer la vitesse d'entrée (concentration dans l'eau ambiante > concentration dans l'eau surnageante) ou de sortie (concentration dans l'eau surnageante > concentration dans l'eau ambiante) des métaux dissous. On a constaté que les enceintes d'aluminium contaminaient l'eau de mer avec du Cd et du Cu. On a mesuré une vitesse nette de sortie ($\mu g.m^{-2}.h^{-1}$) dans le cas du fer (72 to 287), du Mn (5 - 120) et du Zn (-134 to 63), lorsque les sédiments superficiels étaient partiellement ou complètement anoxiques. Le Ni, Cd et le Cu étaient également extraits dans l'eau surnageante, mais la vitesse d'extraction était faible ($<10\ \mu g.m^{-2}.h^{-1}$) et variable. La complexation du Cu par la matière organique dans l'eau de mer et dans l'eau contenue dans les sédiments diminuait l'efficacité d'extraction des colonnes de XE-305; cepedant, il y avait libération de Cu non complexé dans de l'eau peu oxygénée reposant sur des sédiments réduits. Dans le cas de tous les autres métaux dissous, l'efficacité d'extraction était supérieure à 75%. Les vitesses de sortie des métaux contenus dans les sédiments du port d'Halifax sont semblables à celles mesurées dans la baie de Narragansett.

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1 SUMMARY

The objective of the study was to assess a technique for determining the trace metal fluxes between sediments and overlying seawater. The technique consisted of the BIO Benthic Chamber modified to include two Seastar in-situ water sampling units (pump, filter and resin column). If the technique proved viable, it could then be used to measure the flux of metals as dissolved species between sediments and seawater. The technique would be of particular relevance to environmental assessments of contaminated sediments, sediments proposed for dredging and sediments disposed at open-water disposal sites. This report documents the results of the experiments undertaken in 1989, using two sites in Halifax Harbour as test sites.

The study consisted of four experiments:

Exp. #1 A test of the BIO Benthic Chamber to determine if leached metals would be a source of contamination;

Exp. #2 Comparison of the flux of metals as dissolved species occurring at an "impacted" versus an "unimpacted" site;

Exp. #3 Comparison of the change in the dissolved metal flux by altering the oxidation of the surface sediments and the overlying waters at the more contaminated experimental site;

Exp. #4 Test of the column elution efficiencies and elution protocol.

Experiment #1 demonstrated that the Chambers could contaminate the seawater with cadmium and lead. The results of Experiment #2 suggested a higher rate of release from the more contaminated site for iron, manganese and possibly zinc, with the rate of release attributable to anoxic sediments existing at the surface of the sediment; i.e., there was no iron/manganese oxyhydroxide surface layer to control the interaction between the bulk of the sediments and the overlying waters. In Experiment #3, the inducing of significantly reduced oxygen content in the surficial sediments, further promoted the flux of iron, manganese and possibly zinc and

nickel from the sediments. As the oxygen content of the overlying waters was reduced to 20% saturation, the flux rate became more dependent upon the chemistry of the anoxic surface sediments.

There were a number of problems with the experimental system: 1) the Chambers were constructed from polished aluminum which released cadmium and lead into the water contained within the Chamber; 2) the Seastar columns were unable to adsorb complexed copper from natural water systems; 3) the elution protocol recommended by Seastar at first destroyed the chemical nature of the columns and, when modified, required a very cumbersome analytical procedure.

The conclusions of the study are as follows:

1) The experimental system appeared to work and answer the basic objective of providing a system to monitor the flux of dissolved metals from the sediments.

2) The experimental system, as tested, limited the findings of the study. Contamination from the metallic chamber and variable results from the columns, provided results which were difficult to interpret. It is recommended that the experimental system be constructed from Teflon and an alternate to the Seastar resin columns be investigated.

3) There was an efflux of iron and manganese from the sediments into the overlying water column, when the surface sediments are partially or wholly anoxic. It was difficult to determine if the other metals of interest also had an efflux into the water column, although it appeared that zinc, copper and nickel were also being leached when the overlying waters contained a low saturation of oxygen.

4) The fluxes of dissolved metals investigated in Halifax Harbour were similar to those determined for Narragansett Bay sediments. However, neither study was able to ascertain the role of complexation in the flux of such metal contaminants as copper, lead or cadmium.

5) These experiments focussed on trace metals as there was a large data base for Halifax Harbour sediments. There is considerable interest in organic contaminants in the harbour and it is recommended that the technique be tested for organic contaminant fluxes, in particular, of polynuclear aromatic hydrocarbons.

2 INTRODUCTION

2.1 Study Objective

The objective of the study was to assess a technique for determining the trace metal fluxes between sediments and overlying seawater. The technique consisted of the BIO Benthic Chamber modified to include two Seastar in-situ water sampling units (pump, filter and resin column). If the technique proved viable, it could then be used to measure the flux of metals as dissolved species between sediments and seawater. The technique would be of particular relevance to environmental assessments of contaminated sediments, sediments proposed for dredging and sediments disposed at open-water disposal sites. The Terms of Reference for the study are presented in Appendix A.

This report documents the results of the experiments undertaken in 1989 using two sites in Halifax Harbour as test sites.

2.2 Flux of Metals

The flux of trace metals can be affected by a number of factors:

* chemical nature of the metal in the sediments;
* the physical-chemical regime in the sediments;
* the physical-chemical regime in the over-lying waters;
* physical disturbance of the sediments (including bioturbation);

The chemical nature of the metal in the sediments is a function of the source of the metal; the route of input to the sediments; and, the subsequent diagenesis of the material with which the metal is associated. Naturally-occurring metals typically are associated with particular rocks or minerals deposited in the sediments during weathering and erosion of adjacent landmasses.

In contrast, metals from anthropogenic sources can enter the overlying waters by a variety of routes - associated with precipitation from the atmosphere, associated with solid phases or particulate matter, or as dissolved/complexed species in the aqueous phase. Some metals form organometallic compounds, with different chemical and physical properties from metals associated or adsorbed to organic matter. Particulate material settles out at a rate depending on its size and specific gravity; dissolved or complexed metals in the aqueous phase can be adsorbed onto flocculating suspended matter and thus transported to the sediments.

Once in the sediments, shifts in the geochemical associations typically occur due to diagenic reactions as a function of the rates of deposition, biological activity, and the organic content of the depositing material. Anthropogenic metals are associated primarily with organic detritus and fine-grained particulate matter (i.e, particles less than 64 micron in size). Naturally-occurring metals can be distributed throughout the size range of materials as a function of the degree of weathering and physical break-up of the rock.

Typically, sediments consist of a surficial oxidized zone of 2-5 cm in thickness underlain by two zones of anoxic sediments. The depth of the upper anoxic zone is a function of the deposition of organic matter and the resultant micro-biologically mediated reactions. The deeper zone tends to relatively depleted in microbiota reflecting the depletion of chemical sources of oxygen. The flux of metals between the overlying waters and the deeper horizons is then controlled by the physical and chemical regime that exists in the surficial sediments and the adjacent bottom waters, often called the benthic boundary layer.

Water with a good circulation and oxygen content will maintain an oxidized surface layer on the sediments. With oxidation of the surficial sediments, iron and manganese oxyhydroxides are formed that control the chemical mobility of many other trace metals.

In contrast, if the overlying water is relatively stagnant and the sediments contain large quantities of organic matter, the surficial sediments will be anoxic. This alters the chemical regime in the sediments with the solubility of metal sulphides and metallic-organic complexes becoming the controlling mechanisms for metal solubility. Diffusion towards the surface of the sediments

can occur via porewater movement or be induced through physical disturbance or bioturbation of the sediments to horizons as deep as one metre.

Sediments in near-shore environments are typically not uniform in nature or consistency, but a significant "patchiness" or heterogenity occurs as a result of the various input mechanisms. The surface of the sediments can contain zones of oxidized and reduced material. The heterogeneous aspect can be further altered if the overlying waters become anoxic at certain times. Thus the flux of metals for a sediment becomes the "apparent flux" based on a combination of reactions occurring at the same time within a study area.

Some coastal areas and the deep-sea zones typically receive a more uniform sedimentation rate and nature of materials. Therefore the chemistry of the surficial sediments is more uniform and the apparent flux of metals is more uniform.

To measure the apparent net flux of metals as dissolved species to or from sediments, it was proposed to measure the metals in the waters overlying sediments at two sites in Halifax Harbour. The measurement technique was BIO Benthic Chamber modified by the addition of two Seastar in-situ water samplers which would adsorb the dissolved metals.

Under good experimental conditions, the only natural variable should have been the difference in trace metal concentrations, with other variables fixed or controlled by the experiment. The experiments were undertaken in situ; i.e., the sediments remained at their natural site. No attempt was made to control variables such as water circulation, input of anthropogenic materials or biological activity. Thus the flux measured, was an apparent flux for the test site, as it would naturally occur.

One process studied was the leaching of metals from contaminated compared to uncontaminated sediments, while maintaining dissolved oxygen in the overlying water at near saturation. The second process considered the flux of metals from the contaminated sediments when the dissolved oxygen content was significantly reduced.

2.3 Description of Experiments

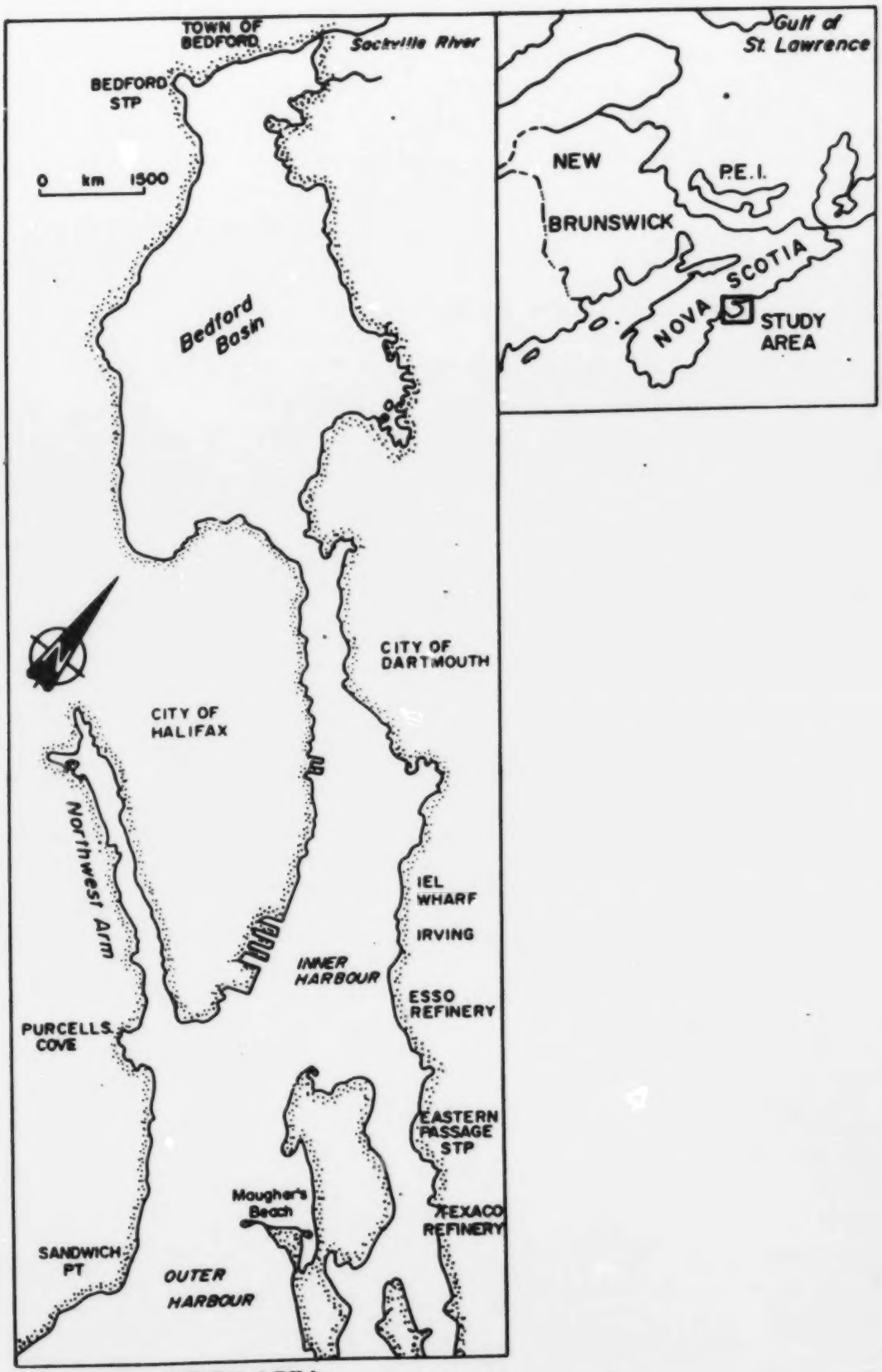
2.3.1 Study Locations

For the purposes of providing a convenient study area, the experiments were conducted in Halifax Harbour using two sites (Figures 1 and 2). The two sites were selected to provide a contrast in experimental conditions, with one site to be "impacted" by anthropogenic metal contamination and the other to be "unimpacted". Using the data from Buckley and Hargrave (1989), Site #1 was located in the area directly off the outfall of the Eastern Passage Sewage Treatment Plant (Figure 3). The Eastern Passage STP receives sewage primarily from residential areas, with minimal commercial or industrial effluent. Site #2 was located in Drake's Gut between Lawlor's and McNab's Islands (Figure 4). The site was defined as "unimpacted" as it was relatively isolated from built-up areas and would receive contamination only as material transported from other parts of the harbour.

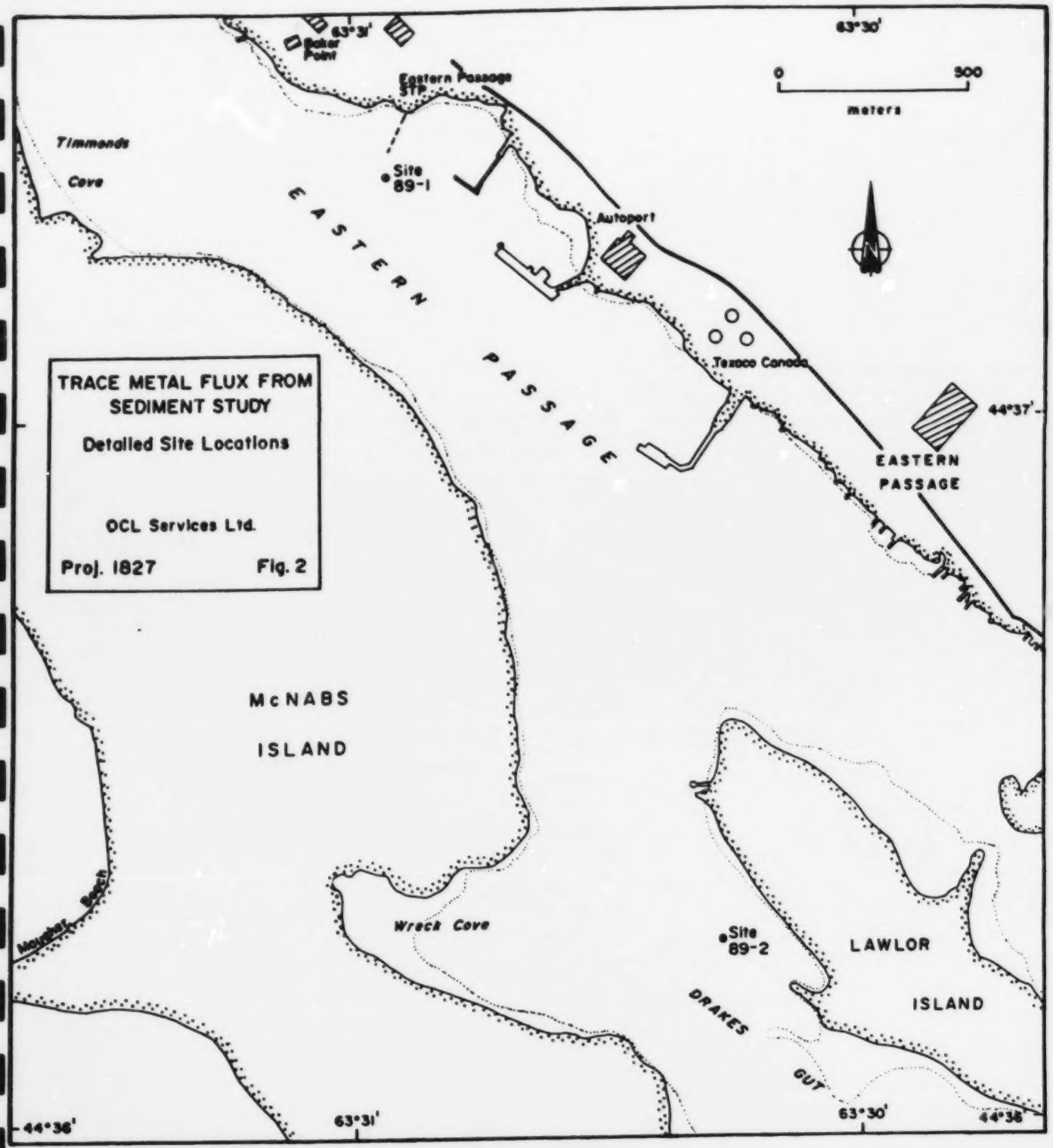
To provide a more detailed characterization of the two study sites, surface sediment grab samples were collected by diver and analyzed for particle size, total organic carbon and trace metals. In addition, small cores were diver-collected and detailed profiles of the dissolved oxygen content determined in DFO laboratories at Bedford Institute of Oceanography.

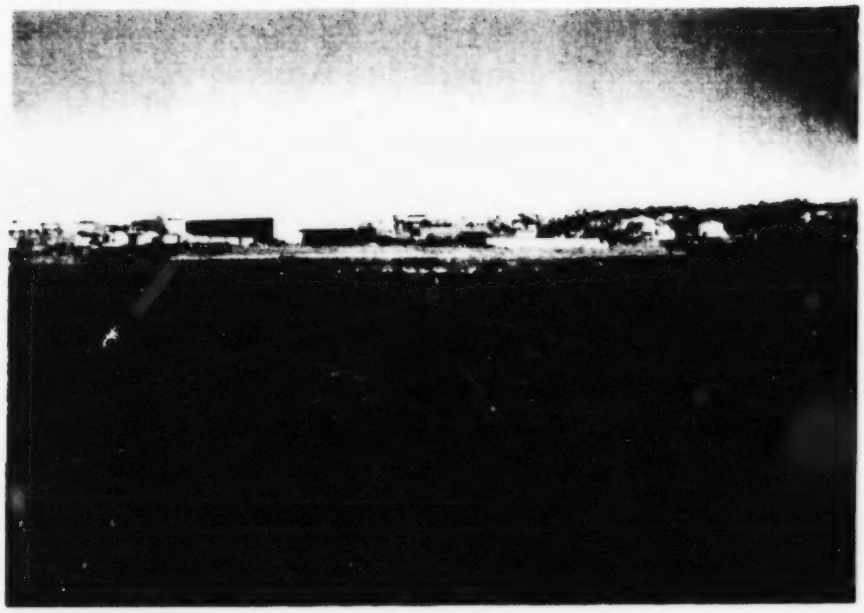
2.3.2 Experimental System

The experimental system consisted of the BIO Benthic Chamber (Hargrave and Connolly, 1978), modified by the addition of two Seastar In-Situ Water Samplers (Figures 5 and 6). At each of the test sites, two systems were deployed to provide experimental duplicates.



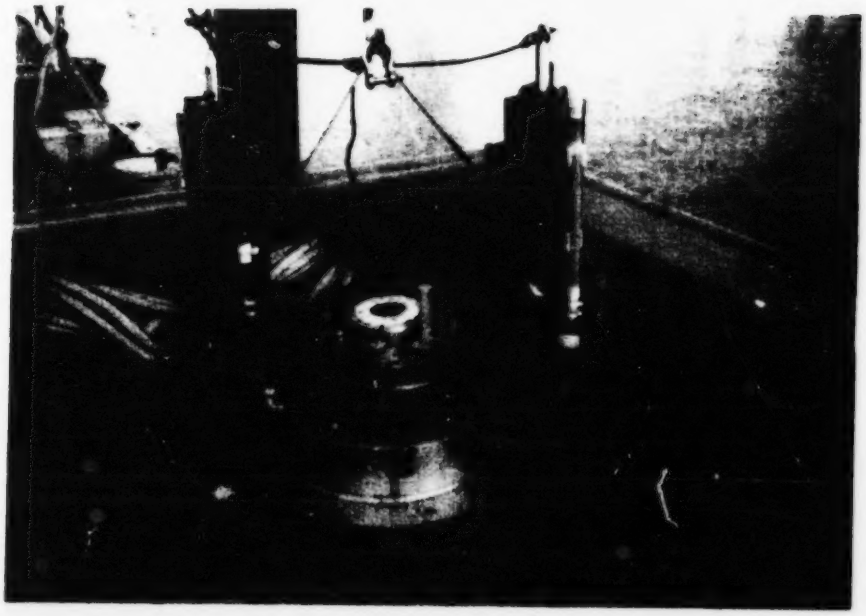
STUDY AREA
FIGURE 1


TRACE METAL FLUX FROM SEDIMENT STUDY
Detailed Site Locations
OCL Services Ltd.
Proj. 1827 Fig. 2
63°31'
Baker Point
Eastern Passage STP
63°30'
0 300
meters
Timmonds Cove
Site 89-1
EASTERN PASSAGE
Autoport
Texaco Canada
44°37'
EASTERN PASSAGE
McNABS ISLAND
Wreck Cove
Site 89-2
LAWLOR ISLAND
DRAKES GUT
44°36'
63°31'
63°30'
44°38'

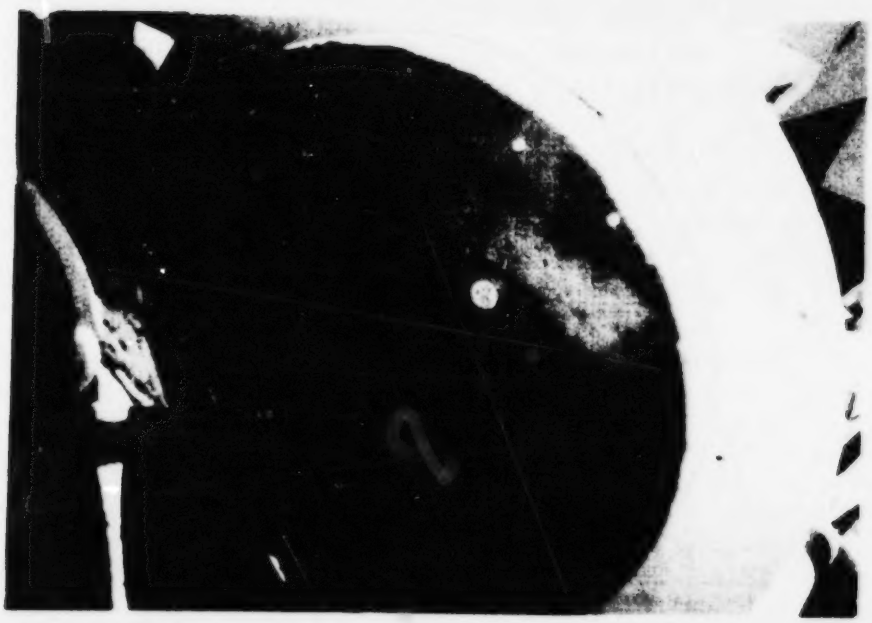


Photograph of Site 89-1 Figure 3

Site 89-2 Drake's Gut Figure 4



Benthic Chamber (top View) Figure 5



Benthic Chamber (bottom View) Figure 6

The BIO Benthic Chamber is constructed of polished aluminum with an enclosed volume of 17.6 L and area of 0.145 m^2. The outer and inner surfaces were spray coated with Nr. 438 Teflon coating (A. W. Chesterton Co., Stoneham, Mass.) To minimize leaching of metals from the aluminum surfaces. Measurement of the dissolved oxygen and redox of the sediments provided a measure of the conditions controlling the flux of metals through the sediment/water interface. To monitor the dissolved oxygen content in the water, a time-operated automatic sampling device was used. The device was activated to collect a sample every three hours during the pumping time. The contents were analyzed within one hour after the completion of the experiment using a Radiometer Blood Gas Analyzer.

To monitor the changes in the trace metal content of the water, two Seastar pumps were mounted on the chamber: one to sample the water enclosed within the chamber; the other to sample the exterior or ambient water. In the Seastar system, the seawater is drawn at a select rate through a cartridge 0.45 micron filter and then a Teflon column filled with 8-hydroxyquinoline immobilized on polystyrene XE-305 resin. The resin adsorbs the dissolved trace metals from the seawater and as large volumes can be pumped through over a 24 hour period, it also concentrates the trace metals in a "sample".

Experimental Design

The study consisted of four experiments:

Exp. #1 A test of the BIO Benthic Chamber to determine if leached metals would be a source of contamination;

Exp. #2 Comparison of the dissolved metal flux occurring at an "impacted" versus an "unimpacted" site;

Exp. #3 Comparison of the change in the flux by altering the oxidation of the surface sediments and the overlying waters at the more contaminated experimental site;

Exp. #4 Test of the column elution efficiencies and elution protocol.

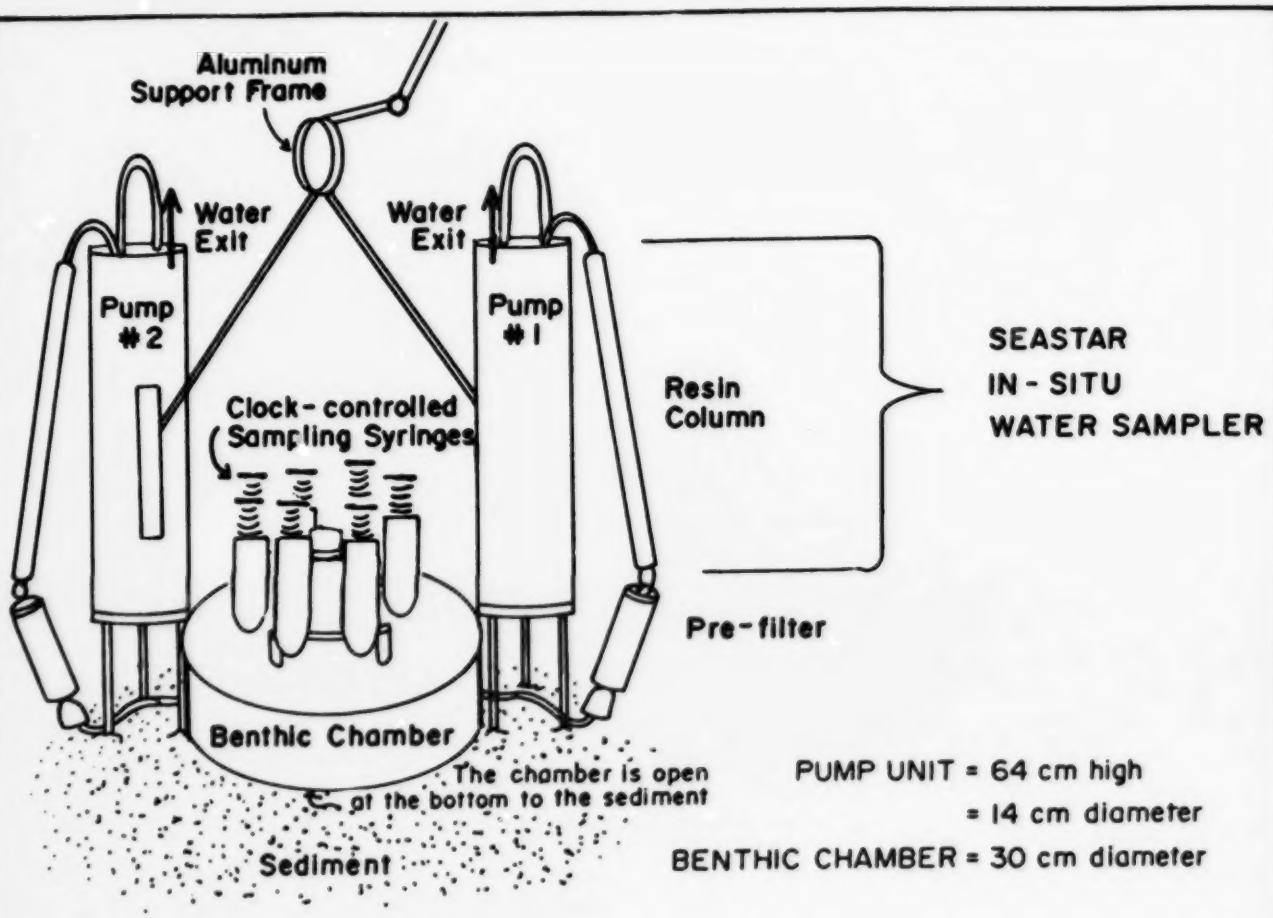
Although the aluminum Chambers had been sprayed with a Teflon coating to minimize contamination, Experiment #1 was a test to determine if contamination was occurring, particularly of the water within the Chamber. These preliminary tests were undertaken in the flowing seawater system at the Bedford Institute.

Figure 7 illustrates the Chamber and the method of sampling the seawater in Experiments #2 and #3.

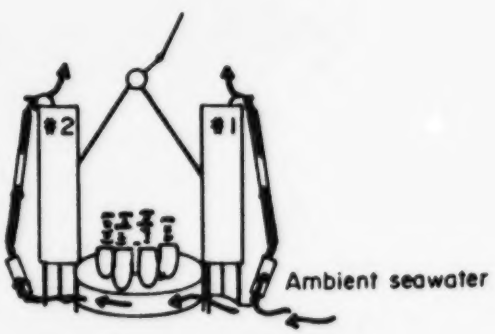
In Experiment #2, one Seastar sampler on each Chamber pumped water from outside of the Chamber (labelled as "ambient seawater"); the other Seastar sampler pumped water from within the Chamber ("labelled as "Chamber seawater"). As the objective of Experiment #2 was to test the flux of dissolved metals from the sediments under natural conditions of oxidized overlying water, a valve on the Chamber was opened to permit external water to circulate through the Chamber, be pumped through the Seastar sampler and then discharged into the surrounding waters.

In Experiment #3, the oxygen content of the overlying water was to be significantly decreased. The experiment was conducted only at Site 89-1. The Chambers were deployed and permitted to be in place for twenty-four hours before starting the Seastar pumps. As illustrated in Figure 7, one Seastar pump sampled the "ambient" seawater, while the other sampled the interior Chamber water. However, in this case, no recharge water was permitted to enter the Chamber. Recognizing that a long pumping time would induce a stress on the flux from the sediments, the pumping time and rate were limited to the 17L of seawater contained within the Chamber.

Continued problems with the apparent inability of the columns to either adsorb or elute copper following the Seastar protocol, led to Experiment #4. Bedford Basin seawater was spiked with a mixed metals standard and eluted with acidic solutions of increasing strengths of acid.

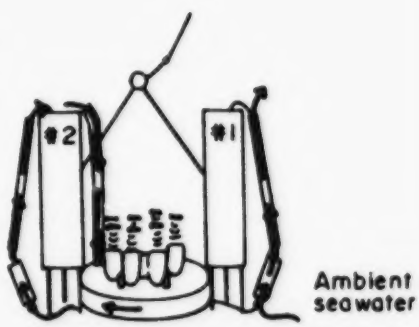


A)



EXPERIMENT 2: CHAMBER WATER CONTINUOUSLY REPLACED BY AMBIENT SEAWATER.

B)



EXPERIMENT 3: CHAMBER WATER RE-CIRCULATING; CHAMBER WATER BECOMES ANOXIC.

TRACE METAL FLUX FROM SEDIMENT STUDY
EXPERIMENTAL SAMPLING CONDITIONS

Project 1827 Figure 7

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3 METHODS

3.1 Trace Metal Analyses of the Seastar Columns

The procedure followed that specified by the manufacturer. A solution of 0.5 N HCl/0.05 N HNO_3 was used to elute the metals off the resin column. This was followed by an extensive washing of the column with distilled-deionized water to rinse the column of acid. The washings were not combined with the initial elution rinse. This was a modification of the original procedure which entailed a follow-up rinse with ammonium hydroxide. This was found to alter the nature of the resin and lead to desorption of the quinoline complexing reagent.

The eluted solutions were analyzed using a Varian atomic absorption spectrometer (SpectrAA-40) in the flame mode, with operating conditions as set by the manufacturer. As the lead concentrations were relatively low, these were determined by flameless atomic absorption spectroscopy. All calibration standards were prepared from a mixed metal standard based on pure 1000 mg/L solutions.

3.2 Sediment Analyses

3.2.1 Particle Size Distribution

The wet sediment was placed in a 250 mL plastic bottle to which was added about 100 mL of deionized water and 10 mL of 30% hydrogen peroxide. This was shaken for twenty four hours on a wrist-action shaker and then heated for several hours to drive off the excess peroxide.

The slurry was stirred and sieved through a 64 micron stainless steel sieve using deionized water. The "fines" passing through the sieve were collected in a 1000 mL graduated cylinder, while the "coarse materials" retained on the sieve were oven-dried. The dried

coarse fraction was sieved through a series of stainless steel sieves mounted on a Ro-tap shaker with sieve divisions of whole phi from -5 to +4. After sieving each fraction was weighed.

To the graduate cylinder was added the material collected in the bottom pan of the sieves (the pan fraction) and a 1% Calgon solution as a peptizing agent. The cylinder was brought up to volume, thoroughly stirred and a series of pipette withdrawals made at fixed periods of time representing the settling rates for the +4 to +9 phi fractions.

The removed material was dried and weighed. The two sets of weights were combined and the frequency distribution plotted against nominal particle diameter on a semi-log plot. The % content of gravel, sand, silt and clay were also calculated.

3.2.2 Total Organic Matter (Loss of Weight on Ignition)

The sample was wet-homogenized and a discrete sub-sample placed in a porcelin crucible. The sample was oven-dried at 105 deg C to remove extraneous water and the dry weight recorded. The sample was then placed in a muffle furnace at 420 deg C for one hour, cooled and weighed. The weight loss was defined as the total organic matter or loss of weight on ignition. Results are reported on a dry weight basis.

3.2.3 Trace Metals

The samples were air-dried for two days at room temperature. They were lightly pulverized in an agate mortar and pestle and then sieved through a 10 mesh (1 mm) stainless steel screen to remove large objects. The samples were dry homogenized and 0.5 g of each sample placed in separate Teflon digestion vessel. To this was added 3 mL of nitric acid, 1 mL of perchloric acid and 3 mL of hydrochloric acid. The sample was digested for three hours at approximately 90 deg C and after cooling, taken to near dryness on a hotplate. The residues were dissolved in 1 N hydrochloric acid and diluted to appropriate volumes in plastic volumetric containers.

The resultant solutions were analyzed for trace metal content by atomic absorption spectroscopy (Varian SpectrAA-40) in either the flame (for Cu and Zn) or flameless modes (Cd and Pb). Each analytical set consisted of 10 unknowns, two replicates and two sediment standard reference materials. Quantitation was made against commercially available standards diluted to the appropriate concentrations. Results were reported on a dry weight basis.

3.2.4 Redox Potential

Redox measurements were made twice:

1) directly after the core was collected by the diver and returned to the surface, the redox potential of the upper 1 cm was measured using a Calomel electrode/ platinum electrode combination;

2) upon return to the DFO laboratory at BIO, using a micro-electrode system connected to a controlled step arm which permitted the measurement of the redox potential throughout the length of the 5 cm cores.

3.3 Dissolved Oxygen of Chamber Water

Using the time controlled sequencing sampler on the Benthic Chamber, water samples from within the chamber were collected every three hours. The dead space in the sampler tips contained mercuric chloride to preserve the samples. The samples were analyzed using a Radiometer Blood Gas Analyzer.

4 RESULTS

4.1 Evaluation of the Sites

The two sites were selected to meet the general criteria of contaminated versus uncontaminated sites, using the data from Buckley and Hargrave (1989). Sediments from the two actual sites were collected and analyzed, with the results given in Table 4-1 (the particle size distribution curves are given in Figures 8 and 9). The temperatures of the seawater and sediment varied from 10 to 12 deg C during the experiments.

Visual examination of the samples in the field indicated that the two samples were fairly similar in consistency. As to be expected, the redox potential for Site 89-1 was more negative (-65 mV) than for Site 89-2 (+137 mV). (Table 4-1).

Subsequent analyses showed that the Site 89-2 sediment had a lower organic matter (19.0 compared to 28.1 g/kg) coupled with a marginally coarser particle size distribution (median particle size of approx. 32 micron compared to 14 micron) for Site 89-1. The data in Table 4-1 also illustrate the differences in the metal content.

Diver observations described the sediments at Site 89-1 as being greyish-black with large white patches of sulphur bacteria. There was ample evidence of sewage outfall jetsam. The surficial sediment of the site is illustrated in Figure 10. In contrast, the sediments at Site 89-2 were fine-grained and black in colour, but there was no flotsam nor sulphur bacteria mats. The surficial sediment of the site is illustrated in Figure 11.

TABLE 4-1

Analyses of Sediments at Two Test Sites

(conc. in dry wt.)

Parameter	Site 89-1 (Eastern Passage)	Site 89-2 (Drake's Gut)
loss of wt. on ign. (g/kg)	28.1	19.0
cadmium (mg/kg)	0.47	0.18
copper (mg/kg)	36.3	11.3
lead (mg/kg)	48.3	14.1
zinc (mg/kg)	103	46.1
gravel (%)	0.0	0.0
sand (%)	8.6	41.5
silt (%)	70.9	48.6
clay (%)	20.5	10.0
median particle size	14 micron	32 micron
E_h (mV) (upper 1 cm):		
on core retrieval	-65 (+/-20)	+137 (+/-15)
in laboratory	-50 (+/-30)	+153 (+/-12)

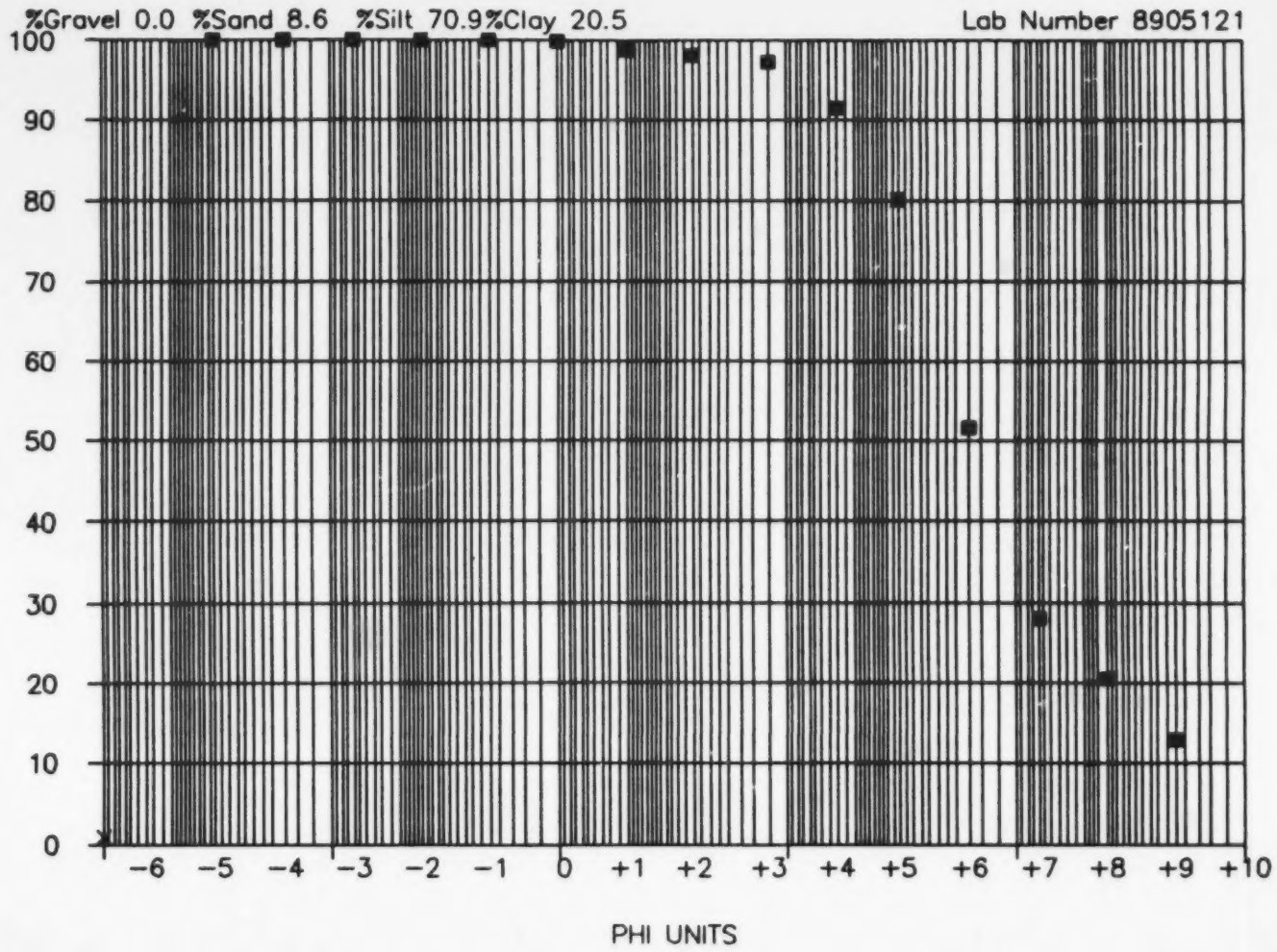

Eastern Passage STP
%Gravel 0.0 %Sand 8.6 %Silt 70.9%Clay 20.5
Lab Number 8905121
100
90
80
70
60
50
40
30
20
10
0
% FINER
−6 −5 −4 −3 −2 −1 0 +1 +2 +3 +4 +5 +6 +7 +8 +9 +10
PHI UNITS

Figure 8

Drake's Gut

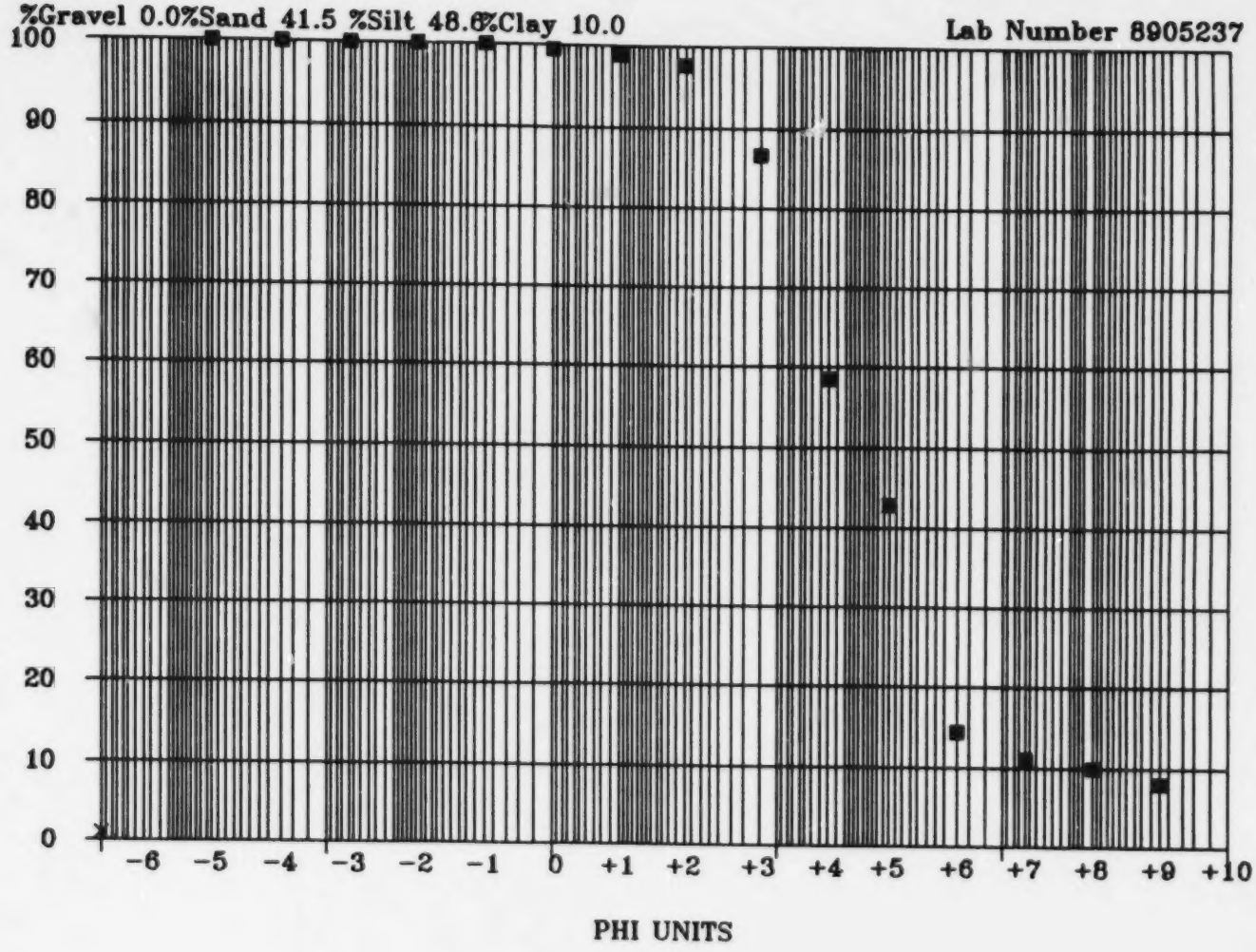
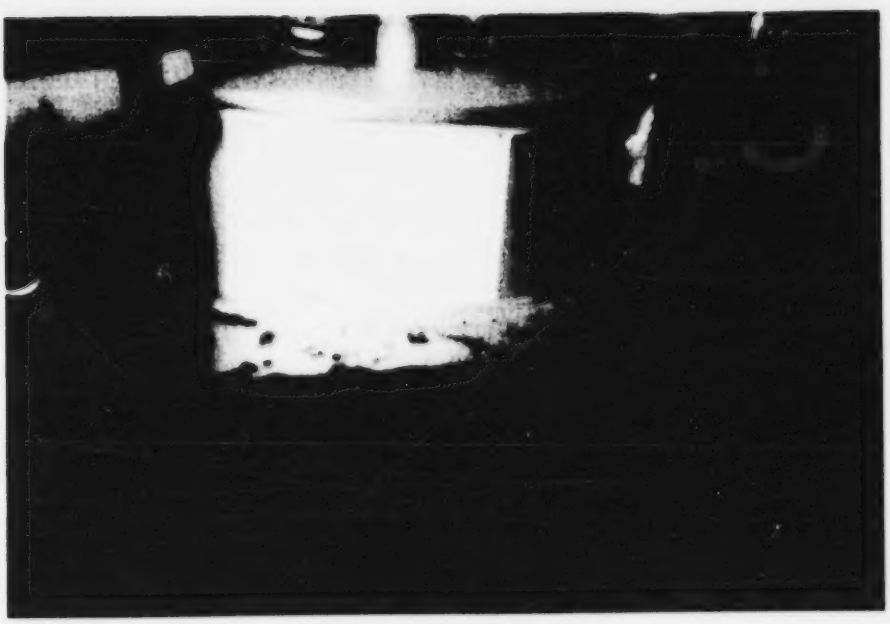


Figure 9

Underwater View of Site 89-1 Figure 10



Underwater Photograph of Chamber
at Site 89-2 Figure 11

4.2 Experiment #1: Effect of Chamber Materials and Testing of Pumps

Experiment #1 was conducted with the objectives of 1) testing the impact of using the aluminum chambers on the trace metal concentrations measured in the ambient waters; and, 2) to test the Seastar pumps. For convenience, the experiment was conducted at BIO. The chambers were deployed in tanks of running seawater with no sediment present. The pumps were allowed to run for 24 hours at a rate of 50 mL per minute.

The results are presented in Table 4-2. To assess the results, comparison was made to analyses of the tank seawater as undertaken by J. Dalziel, Marine Chemistry group, BIO. The experiments showed:

1) lead and cadmium were leached from the chambers;

2) copper either was not adsorbed by the resin column or not eluted following the Seastar elution procedure;

3) iron, manganese, zinc and nickel potentially could be used as monitoring parameters for the subsequent field experiments.

At this time, difficulties were also encountered with the resin column elution protocol as provided by Seastar. After discussions with them, the procedures following the acid elution was changed to the use of large volumes of distilled-deionized water rather than an alkali solution to restore the column pH to conditions acceptable for trace metal adsorption. Using the original protocol seriously damaged the column resins and required the manufacturer to replace the columns before the remainder of the experiments could be undertaken.

Table 4-2

Results of Experiment #1: Chamber Testing

(conc. in ug/L)

Code	Col. No.	Date	Vol. (L)	Flow (mL/min)	Cd	Cu	Pb	Zn	Fe	Mn	Ni
BTH-A-A	327	Oct. 2-3	212	149	0.09	-	0.05	21	0.18	0.34	0.27
BTH-B-C	323	Oct. 2-3	133	94	0.27	0.01	0.09	18	0.28	0.53	0.27
BTH-C-A	319	Oct. 3-4	55	96	0.23	0.01	0.07	69	0.32	0.77	0.27
BTH-D-C	328	Oct. 3-4	133	113	0.30	0.02	0.09	55	0.13	0.44	0.28
BTH-A-A*	318	Oct. 4-6	139	49	0.19	<0.01	0.06	73	0.21	0.33	0.22
BTH-B-C*	322	Oct. 4-6	139	48	0.47	<0.01	0.07	70	0.15	0.29	0.20
Tank Water* (Oct. 6)					0.45	1.71	0.10	85	-	-	-
Harbour Water* (Mean of Mar., May, June/89)					0.035	0.41	0.03	4	2.2	1.7	0.5

*Analyses provided by J. Dalziel, Marine Chemistry, BIO

-A = ambient water; -C = water from within chamber

4.3 Experiment #2: Comparison of Uncontaminated to Contaminated Sediments

At each site, the modified chambers were deployed in duplicate. Deployment was undertaken by divers working off the **R. V. Sigma T** at Site 89-1 and the **R. V. Navicula** at Site 89-2. The divers ensured that the Chambers were gently lowered to the bottom without undue sediment disturbance and that the pumps were working properly. A large flotation device was deployed to mark the site. The chambers were deployed for a period of twenty-four hours and then retrieved. The experiment at Site 89-1 was conducted on Oct. 23-24/89; at Site 89-2 on Nov. 6-7/89.

At Site 89-1, the pumps were operated at a rate of 50 mL per minute. The rate was chosen on the basis of preliminary data supplied by J. Dalziel for concentrations in the harbour waters (Table 4-3) and the detection limits as set by use of flame atomic absorption spectroscopy.

Suspecting that the concentrations at Site 89-2 were likely lower than at Site 89-1, the rate was increased to 150 mL/min for an overall volume of approximately 260 L being pumped.

During the deployment of the Chambers, staff from BIO using a modified General Oceanics Go-Flo water sampler collected water at mid-depth. Analysis of these samples provided a ground-truthing to test the "ambient" water concentrations measured using the Seastar sampler system.

The results of the experiment are given in Tables 4-4 and 4-5.

TABLE 4-3

Metal Concentrations in Harbour Seawater

(conc. in ug/L) *

Date	Cd	Cu	Pb	Zn	Fe	Mn	Ni
Oct. 24-a	0.018	0.30	0.036	6.6	5.0	3.2	0.35
Oct. 24-b	0.024	0.30	0.047	7.7	5.0	2.0	0.37
Oct. 24-mean	0.021	0.30	0.042	7.2	5.0	2.6	0.36
Nov. 7-a	0.023	0.43	0.159	4.6	4.9	2.5	0.64
Nov. 7-b	0.029	0.46	0.159	3.7	5.2	2.9	0.66
Nov. 7-mean	0.026	0.45	0.159	4.1	5.1	2.7	0.65
Nov. 17-a	0.026	0.52	0.252	7.2	3.8	2.4	0.50
Nov. 17-b	0.037	0.51	0.252	8.8	3.5	2.4	0.54
Nov. 17-mean	0.032	0.52	0.252	8.0	3.7	2.4	0.52
Range (min/max)	0.021-0.032	0.30-0.52	0.042-0.252	4.1-8.0	3.7-5.0	2.4-2.7	0.36-0.65

*All samples filtered through 0.45 micron; analyses provided by J. Dalziel, BIO

TABLE 4-4

Results of Experiment #2 (Oct. 22-23/89)
Site 89-1 (Eastern Passage STP)

(conc. in ug/L; corrected for field blank)

Code	Cd	Cu	Pb	Zn	Fe	Mn	Ni
Ambient (#320)	0.022	0.020	0.013	1.549	0.232	2.101	0.170
Chamber (#326)	0.123	0.032	0.011	1.853	2.261	3.239	0.169
Chamber (#324)	0.133	0.032	0.014	2.565	1.398	4.040	0.136

(assuming 100% recovery in the elution)

4.4 Experiment #3: Effect of Inducing Anoxic Surface Sediments

Experiment #3 was conducted only at Site 89-1. The Chamber system was deployed in duplicate by divers operating from the **M.V. Dive-Com III**.

To induce anoxic surface sediments before proceeding with the experiment the units were deployed on Nov. 16/89. The pumps were activated to permit circulation of the water within the chamber, but no "new" water was introduced from outside nor was the water passed through the filter/resin column system. On Nov. 17/89, the divers altered the flow pattern of the water through the Seastar system so that the water now passed through the resin columns. The pumps were operated for two hours at a rate of 150 mL/min. This was calculated to permit all of the water within the chamber to make one pass through the resin column. The other column pumped ambient seawater. Unfortunately, due to vandalism, only one of the Chamber systems was useable on Day 2.

Figure 12 illustrates the nature of the sediment immediately after recovery of the Chamber. The surface sediments had essentially become anoxic; the overlying water was found to contain about 20% saturation oxygen content.

The results of the experiment are given in Table 4-6.

4.5 Experiment #4: Investigation of Problem of Elution of Copper from Seastar Resin Columns

The question of inefficient elution of copper from the resin columns during the experiments led to Experiment #4. A test solution was prepared by spiking Bedford Basin seawater with a series of mixed metal standards using as a base 1000 mg/L inorganic standard solutions routinely used to prepare calibration standards for the metal analyses. As the resultant solution was acidic, the pH was adjusted to 8.3, using ammonium hydroxide. The test solutions were then passed through the resin columns and samples taken to determine the efficiency of retention and elution.

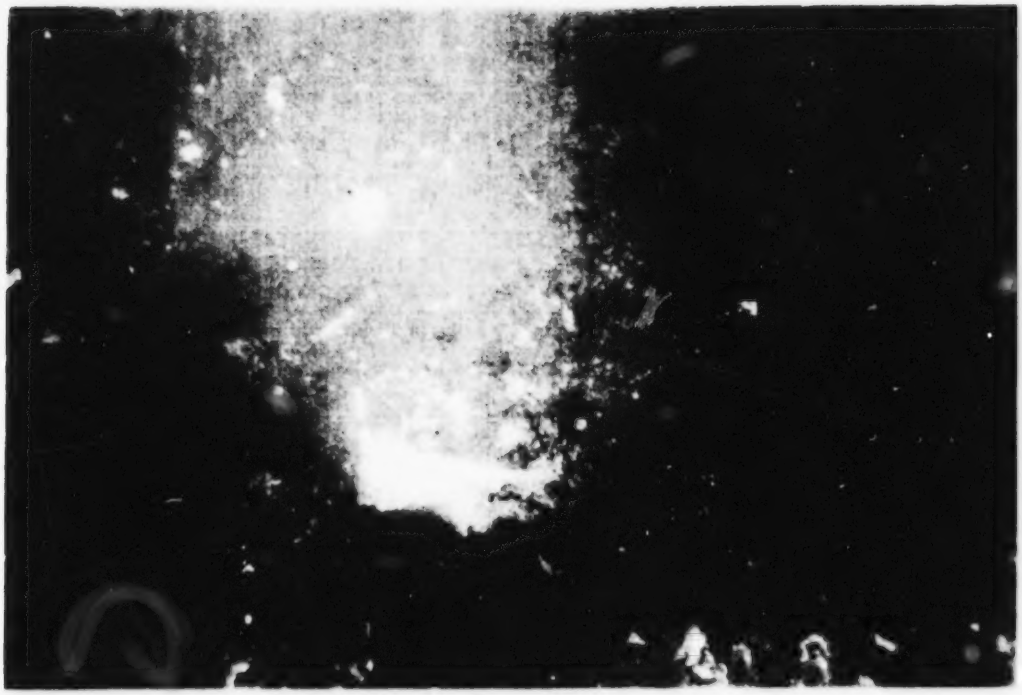
TABLE 4-5

Results of Experiment #2 (Nov. 6-7/89)
Site 89-2 (Drake's Gut)

(conc. in ug/L; corrected for field blank)

Code	Cd	Cu	Pb	Zn	Fe	Mn	Ni
Ambient (#338)	0.0143	0.051	0.024	2.18	1.82	2.37	0.24
Ambient (#337)	0.015	0.037	0.011	3.84	2.36	2.54	0.24
Chamber (#335)	0.010	0.073	0.016	1.50	72.79	3.30	0.22
Chamber (#325)	0.008	0.005	0.003	0.84	6.73	0.90	0.17

(assuming 100% recovery in the elution)



Underwater View of Site 89-1
After Removal of Chamber

Figure 12

TABLE 4-6

Results of Experiment #3 (Nov. 16-17/89)

(conc. in ug/L; corrected for field blank)

Code	Cd	Cu	Pb	Zn	Fe	Mn	Ni
Ambient (#341)	0.025	0.624	0.046	0.72	0.87	1.05	0.31
Ambient (#336)	0.011	0.087	0.011	1.14	0.65	1.25	0.22
Chamber (#339)	0.009	0.936	0.057	1.26	21.94	2.04	1.38

(assuming 100% recovery in the elution)

The Seastar column was rinsed with deionized water (100 mL) to remove excess salts and then eluted with successive 250 mL aliquots of HCl/HNO_3 in strengths of 0.5N/0.05N, 1N/0.1N, and 2N/0.2N. An equilibration time of at least one hour was allowed between successive elutions of the column.

As this was an experiment, the copper levels were much higher than would be expected in the actual seawater samples. Also the copper was added to the seawater as an inorganic solution.

The results of the experiment are given in Table 4-7. In the procedure, a litre of spiked seawater was placed on the column (Test solution #1) and then eluted with approximately 250 mL of acid (Test solution #4). This elution should nominally have yielded a concentration of four times the initial solution concentration. Also the subsequent rinse concentrations should have been low to negligible. This was true for most of the metals, with the exception of copper.

Allowing for some discrepancies in the mass balances, attributed to the variance in salt matrix background, the extraction and elution efficiencies for all of the metals tested were greater than 90%. Although the elution recovery for copper is poorer than for the other metals (86% total recovery), a large proportion is recovered. However this suggests that additional work still is required on the copper procedure.

TABLE 4-7

Results of Experiment #4

(conc. in ug/L)

Test*	Cd	Cu	Pb	Zn	Fe	Mn
1	0.492	4.28	5.40	2.31	2.0	1.0
2	<0.005	<0.005	0.16	<0.005	<0.02	0.164
3	<0.005	<0.005	0.14	<0.005	<0.02	0.031
4	<0.005	<0.005	<0.02	<0.005	<0.02	0.005
5	1.79	7.53	18.9	7.71	6.2	2.87
6	0.112	4.63	0.26	0.055	0.22	0.043
7	0.013	1.79	<0.02	<0.005	0.11	0.017
8	0.006	0.431	<0.02	<0.005	0.05	<0.005

*Test 1 Spiking solution

Test 2 Taken during adsorption (250 mL point)

Test 3 Taken at end of adsorption to test for breakthrough

Test 4 Taken at end of distilled water rinse

Test 5 integrated 265 mL sample; elution of 0.5N HCl/ 0.05N HNO_3

Test 6 integrated 265 mL sample; elution 1.0 N HCl/ 0.1N HNO_3

Test 7 integrated 217 mL sample; elution 2.0 N HCl/ 0.2N HNO_3

Test 8 200 mL rinse at end (contains some 2 N acid mixture)

5 DISCUSSION

5.1 Metal Fluxes to Harbour Waters

Although the major objective of the study was the assessment of the monitoring technique, the measured data can also be used to assess the flux of metals into (or from) the harbour waters.

The solubilization and release of metals to the overlying waters is a very complex chemical process; further complicated for the case of a sediment with mixed oxidized/anoxic sediments. In an oxidized water column, most metals are adsorbed to organic particulate or to particulate formed by iron/manganese oxyhyroxides. The deposition of the metals in the sediment becomes a function of the behaviour of these particles. In anoxic sediments, metals such as zinc, copper, lead and cadmium become immobilized as relatively insoluble sulphides, while metals such as iron and manganese are altered from insoluble oxides to soluble sulphides and are therefore released to the overlying waters.

In studies of metal fluxes from anoxic sediments under controlled laboratory conditions, various authors (e.g., Lu and Chen, 1977; Gambrell et Al., 1982; Hunt and Smith, 1982) have shown that oxidation of the sediments can lead to the release of such metals as zinc, copper, cadmium, or lead. This contrasts with the results reported by Jones and Lee (1978) which showed that in the elutriate test, little or no release of metal contaminants occur when anoxic contaminated sediments are mixed with seawater under well-oxidized conditions.

It is likely that in the real world situation, where anoxic sediments are in direct contact with oxidized overlying waters, the iron and manganese sulphides are solubilized and released into the water column. In oxidized overlying waters, the two metals readily form oxyhydroxides and are re-precipitated to the sediments. The presence of an oxidized overlying water mass thereby creates a sediment boundary layer of iron/manganese oxyhydroxides overlying anoxic sediments.

This boundary layer in turn controls the outward flux of other metals; first by maintaining the anoxic nature of the underlying sediments; and second, by providing a layer through which the other metals must pass and in which they are readily adsorbed by the iron and manganese compounds, as occurs in the water column.

The two sites examined in this project contained very complex sediments. At both sites, there was a layer of surficial sediment which was oxidized by the overlying waters and therefore provided a controlling boundary layer. However, particularly at Site 89-1, there were also areas of anoxic sediment directly exposed to the overlying waters.

It is suggested that in the zones where there was a boundary layer of oxidized sediments, release of metals other than iron and manganese was limited by the boundary layer. In the zones where the anoxic sediments were in direct contact with the overlying waters, iron and manganese were solubilized; the other metals were immobilized by the formation of insoluble sulphides. The inducement of an anoxic sediment surface layer in Experiment #3 further illustrated the trend of solubilization of the iron and manganese from anoxic sediments. Differences between ambient and chamber concentrations in Experiment #2 were attributed to a decrease in the oxygen content of the chamber water due to a slowing of circulation of the water overlying the sediments within the chamber.

The sediments at Site 89-1 are further complicated by the nature of the organic matter in the sediments and the incoming effluent stream. It is likely that metal-ligand complexes are formed in the interstitial waters of the sediments. Such compounds are relatively soluble and could lead to the effective release of the metals into the overlying waters.

However, as discussed in Section 5.3, the monitoring technique did not adsorb complexed metals (e.g., copper) and therefore would not have been able to assess the role of complexation in metal flux.

5.2 Metal Fluxes

In Experiment #2, there was an efflux of zinc, iron and manganese, at Site 89-1, whereas at Site 89-2, there was an influx of zinc, and the fluxes for iron and manganese were variable. There may have been an efflux of copper, but based on the problems found in

Experiment #1, the copper data was suspect. Nickel showed a small influx at both stations but no lead flux occurred. Although cadmium was released at Site 89-1 and low rates of uptake occurred at Site 89-2, flux rates could be unreliable due to chamber contamination. However, concentrations of cadmium and lead in water within chambers were not increased to the degree expected from Experiment #1. This may have been due to the shorter experimental times in Experiment #2.

Experiment #3 clearly showed an efflux of zinc, iron, nickel and manganese with the inducement of low oxygen conditions. Although the copper data is suspect, there was a net efflux. This measurable difference is attributed to the dissolution of ionic species of copper, which had not yet been complexed. As in Experiment #2, the "Chamber" concentrations of lead and cadmium were lower than would be expected from the results of Experiment #1. It is suggested that the degree of contamination was not as bad as had been predicted from the longer time intervals used in Experiment #1.

Experiment #4 illustrated the problem of elution of the natural seawater copper compared to the elution of ionic copper spiked in a seawater. It also illustrated that even with adsorption of ionic copper, the initial elution solution was only 50% effective and that two additional elutions with stronger strengths of acid were required to achieve even a reasonable degree of copper desorption. Additional work is clearly required before the columns can be used for monitoring copper in seawater.

Using an area of 0.145 m^2, and a test time of 24 hours, flux rates were calculated and are presented in Table 5-1. Positive flux rates are into the water column; negative rates are into the sediments.

For comparison purposes, data for Narragansett Bay (Hunt and Smith, 1983) have been included in Table 5-1. Narragansett Bay is of interest to studies in Halifax Harbour because of the similarities in the harbours in the problem of sewage treatment and contaminated sediments. The comparability of the data suggests that the geochemical regimes within the two harbours are similar. In both cases, anoxic sediments are permitting the release of iron and manganese to the overlying waters, while the formation of insoluble metallic sulphides immobilizes metals such as zinc, copper and lead. However, even where the sediments appear to be anoxic, a low rate of positive flux of metals from the sediments to the overlying water

Table 5-1

Calculated Flux Rates

(values in ug/m^2/hr) *

Metal	Halifax Harbour	Narragansett Bay **
cadmium	-0.4 to 7	-0.1 to 5
copper	-2 to 6	-0.05 to 6
iron	72 to 287	0.5 to 419
lead	-1 to 0.2	0.4
manganese	5 to 120	18 to 27
nickel	0 to 7	ND
zinc	-134 to 63	ND

Rates calculated from data in Tables 4-4; 4-5; and 4-6.

* positive values represent flux to the water; negative, to the sediments

** from Hunt and Smith, 1983

column can occur. This reflects both the complex chemical regime in the surficial sediments and the dynamic nature of the sediment/seawater interactions.

5.3 Viability of Test Technique

The prime objective of the study was to assess the application of the Benthic Chamber and the Seastar resin columns technique to determine the flux of dissolved metals from sediments. As this study was considered an experiment, available equipment was used without modification.

The results of Experiment #1 showed that there was a probable release of cadmium and lead from the Benthic Chamber materials. On the basis of this experiment it was decided that the flux measurements for the two metals would be suspect, however, all testing included analyses for these metals.

Although the manufacturer indicated that the resin columns should be able to readily adsorb the metals of interest, in particular copper, it was found that in real-world cases much of the copper existed in a complexed form which could not be adsorbed by the column. It is possible that the same was true fro other metals. Comparison of spot samples collected at the time of the experiments (Table 4-3) yielded trace metal concentrations that were generally similar to those reported by Dalziel et al., (1989). However, concentrations determined in ambient water using XE-305 columns (Tables 4-4, 4-5, 4-6) were consistently lower than concentrations measured by direct seawater extraction (Table 4-3). Metals that re organically complexed or in a colloidal state in seawater may not be efficiently extracted by the XE-305 columns.

It is recommended that the metal Benthic Chamber be limited to studies involving organic contaminants and that a plastic (preferably Teflon) chamber be constructed for future metal monitoring.

Additional research is required to identify a resin column which can adsorb both free and complexed metal species in seawater. This will be particularly necessary in harbour waters with a high concentration of complexing organic compounds.

5.4 Conclusions

The conclusions are as follows:

1) The experimental system appeared to work and answer the basic objective of providing a system to monitor the flux of dissolved metals from or into the sediments.

2) The experimental system, as tested, limited the findings of the study. Contamination by cadmium and lead from the metallic chamber and variable results for copper, provided results for these metals which were unreliable. It is recommended that the experimental system be constructed from Teflon and an alternate to the Seastar resin columns be investigated.

3) There is a net efflux of iron, manganese, and zinc from the sediments into the overlying water column, when the surface sediments are partially or wholly anoxic. It was difficult to determine if the other metals of interest also had a positive flux into the water column, although it appeared that nickel, and in Experiment #3, copper were being leached.

4) The flux rates for the metals investigated in Halifax Harbour were similar to those determined for Narragansett Bay sediments. However, it is likely that neither study was able to ascertain the role of complexation in the solubilization of such metal contaminants as copper, lead or cadmium.

5) These experiments focussed on trace metals, as there was a large data base for Halifax Harbour sediments. There is considerable interest in organic contaminants in the harbour and it is recommended that the technique be tested for organic contaminant fluxes, in particular, of polynuclear aromatic hydrocarbons.

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APPENDIX A

01 Title: Halifax Harbour Sediment Trace Metal Leaching Study.

Scope of Work:

DFO's role in monitoring environmental quality of inshore marine waters includes the development and testing of new methods to measure sediment-water interactions and processes where contaminants are exchanged between sediments and overlying water. This contract is to provide field assistance and analytical work-up of samples to test the application of a new method to measure the net flux of trace metals (copper, cadmium, zinc, nickel, lead, iron, and manganese) between sediments and overlying water in Halifax Harbour.

Sampling will be carried out by DFO staff during August 1989 from the SIGMA-T in Bedford Basin and Halifax Harbour. Two sites will be selected for deployment of benthic chambers and two attached submersible pumps. One pump will circulate ambient water, while the second pumps water at a pre-set rate which determines the residence time of water in the chamber. Hydroxyquinilone ion exchange resin cartridges will be attached to each pump to strip trace metals from the water. Based on a pumping rate of 100 mL/min., and reported concentrations of trace metals in seawater in Halifax Harbour at Dartmouth Cove and Georges Island, a 24-h pumping period will be carried out at each of two stations. Four replicate experiments will be carried out to produce a total of 16 columns for analyses. Four additional columns unattached to pumps will serve as blanks.

All field equipment for this work will be provided by DFO, Biological Sciences Branch. The resulting ion exchange columns (16 experimental, 4 blanks) will be eluted with 250-50 mL of acid to prepare samples for analyses by flame or flameless atomic absorption spectroscopy for the elements - copper, cadmium, zinc, nickel, lead, iron, and manganese. Concentrations will be reported as µg/L (ppb), taking into account volumes of water extracted during each experiment.

Field work will be carried out by staff from DFO accompanied by one person from the contracting company who will assist during field experiments. Divers needed to place benthic chambers will be provided by DFO.

Duration: Work will begin during the first week of August 1989 and will be completed by the end of August 1989. A period of one month from receipt of ion exchange columns (September 1, 1989) should be sufficient to complete trace metal analyses. Results are to be written-up as a report combined with other information from preliminary experiments and background data on trace metal concentrations in the water column at the study sites in a format suitable for submission to the Regional Ocean Dumping Advisory Committee.

APPENDIX B:

SECTION 1
INTRODUCTION TO YOUR SEASTAR IN SITU WATER SAMPLER

1.1 MAIN FEATURES

Congratulations on purchasing the world's most advanced water sampling system.

The Seastar In Situ Water Sampler (Figure 1) turns to advantage two major developments of the last decade: microprocessors and extraction columns. The microprocessor allows sampling to be carried out according to any desired routine or schedule, monitors and maintains the flow rate, and shuts the instrument down in the event that accumulated particulate causes a substantial drop in flow rate. The extraction columns have the advantage that it is no longer necessary to collect water: the water is extracted In Situ, and the trace constituents are preconcentrated ready for analysis.

The result is a compact, self-contained instrument that has unprecedented flexibility of use and is capable of obtaining uncontaminated samples from large volumes of water.

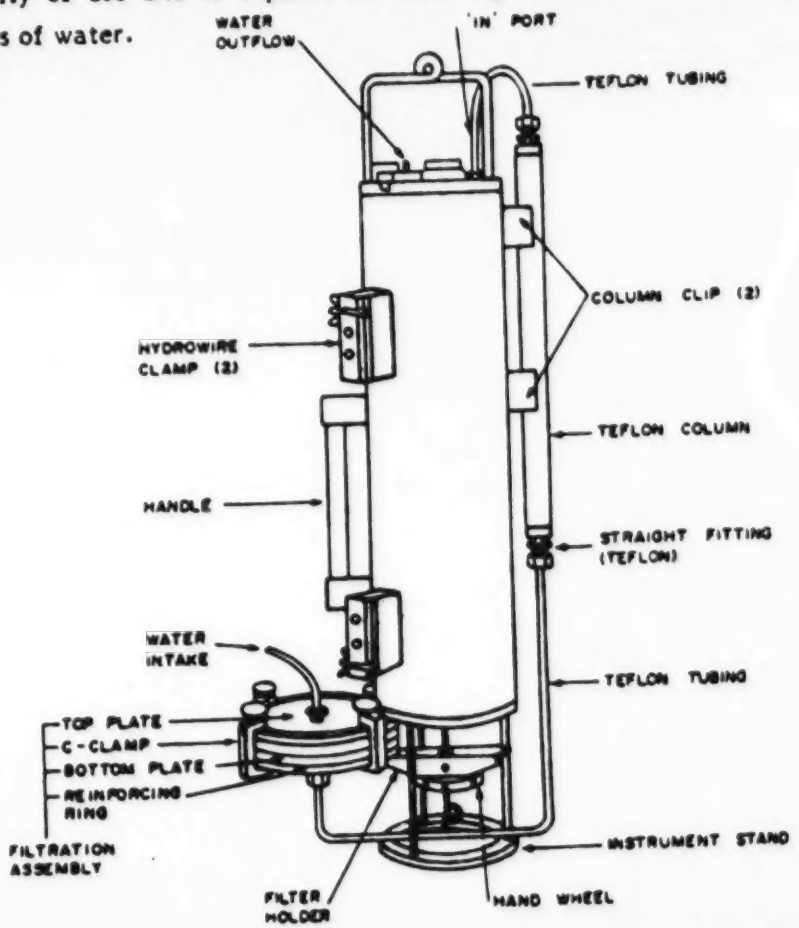

Figure 1. Diagram of the In Situ Water Sampler